Message

From: Zhang, Zhenfa [zhenfaz@email.unc.edu]

Sent: 1/29/2019 2:42:26 PM

To: Strynar, Mark [/o=ExchangeLabs/ou=Exchange Administrative Group

(FYDIBOHF23SPDLT)/cn=Recipients/cn=5a9910d5b38e471497bd875fd329a20a-Strynar, Mark]; Bodnar, Wanda M

[wanda_bodnar@unc.edu]; Surratt, Jason D. [surratt@unc.edu]

CC: Lang, Johnsie [/o=ExchangeLabs/ou=Exchange Administrative Group

(FYDIBOHF23SPDLT)/cn=Recipients/cn=b220365e540947f7a7c55cde0904f73e-Lang, Johns]

Subject: RE: update on synthesis

No problem for me at all. I have to note that now all my product is in water solution though, as our freeze dryer lid broken yesterday when I was trying for a final run of freeze dry. That won't matter for a sample to you for HRMS work. Zhenfa

From: Strynar, Mark <Strynar.Mark@epa.gov> Sent: Tuesday, January 29, 2019 8:55 AM

To: Zhang, Zhenfa <zhenfaz@email.unc.edu>; Bodnar, Wanda M <wanda_bodnar@unc.edu>; Surratt, Jason D.

<surratt@unc.edu>

Cc: Lang, Johnsie < lang.johnsie@epa.gov>

Subject: RE: update on synthesis

Zhenfa,

Can we get a small subsample of the 2 grams to do some HRMS work on it as well?

Mark

From: Zhang, Zhenfa <<u>zhenfaz@email.unc.edu</u>> Sent: Monday, January 28, 2019 9:06 PM

To: Bodnar, Wanda M < <u>wanda bodnar@unc.edu</u>>; Surratt, Jason D. < <u>surratt@unc.edu</u>> **Cc:** Strynar, Mark < <u>strynar.mark@epa.gov</u>>; Lang, Johnsie < <u>lang.johnsie@epa.gov</u>>

Subject: Re: update on synthesis

That is great. So I don't need to request internal standard for purity calculation then. I can wait until the product from Synquest to compare with mine side by side when this is needed. As it current stands, I got around 2 gram of product and I calculated the residue solvent to be a few percent of the nafion BP2 by weight through proton NMR, but I don't know the actual content of the byproduct itself, even though I know the product is there as the major content. To quantify that through 19F NMR is what I intended for an additional internal standard. I have another perfluoro material for the synthesis of Nafion byproduct 2, which could be used as an internal standard, however, the material cane to me with some extra solid suspension. I didn't care about that as a starting material for the synthesis, but I am a little hesitate to use that as a pure standard for purity calculation.

Zhenfa

From: Bodnar, Wanda M

Sent: Monday, January 28, 2019 5:27:51 PM

To: Surratt, Jason D.; Zhang, Zhenfa Cc: Strynar, Mark; Lang, Johnsie Subject: RE: update on synthesis

Also, Rebecca Fry's team said that they placed an order for Nafion BP2 from Synquest who will synthesize ~5g for \$2,000

Wanda M. Bodnar, PhD NC PFAST Network Scientific Program Analyst Dept. of Environmental Sciences & Engineering University of North Carolina at Chapel Hill 162A Rosenau Hall, CB#7431 Chapel Hill, NC 27599 (919) 843-0182

Preferred pronouns: she, her, hers

From: Surratt, Jason D. <<u>surratt@unc.edu</u>> Sent: Monday, January 28, 2019 4:20 PM To: Zhang, Zhenfa <zhenfaz@email.unc.edu>

Cc: Strynar, Mark <Strynar.Mark@epa.gov>; Lang, Johnsie <lang.johnsie@epa.gov>; Bodnar, Wanda M

<wanda_bodnar@unc.edu>
Subject: Re: update on synthesis

Thanks for copying me Mark and Zhenfa. Mark, Zhenfa has been very hard at work on this. However, I'm glad to see you guys are chatting about sharing potential intermediates.

Mark, we will definitely keep you posted. Glad to see you guys are back at work. Sorry for the long shutdown....

Sincerely, Jason

Jason D. Surratt, Ph.D.

Professor

Program Director of the N.C. Per- and Polyfluoroalkyl Substance Testing (PFAST) Network

Co-Director, Undergraduate Studies, Environmental Sciences & Engineering

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On Jan 28, 2019, at 3:59 PM, Zhang, Zhenfa <<u>zhenfaz@email.unc.edu</u>> wrote:

That would be great, thanks. The chemistry and physical chemical property of fluorinate compounds are very special and different to most of other material. If we could get access to some of the intermediate through the person, that would make some of the synthesis easier. For example for those polyethers, I don't see much report at all except a couple of old patents. I have no idea where to get some intermediates if we are going to make some of them and I don't see a practical way to make those intermediate in a lab. Thank you anyway,

From: Strynar, Mark < Sent: Monday, January 28, 2019 12:14 PM

To: Zhang, Zhenfa <zhenfaz@email.unc.edu>; Surratt, Jason D. <surratt@unc.edu>; Lang, Johnsie

<lang.johnsie@epa.gov>

Cc: Bodnar, Wanda M < wanda bodnar@unc.edu>

Subject: RE: update on synthesis

Zhenfa,

Zhenfa

I have a contact who is a retired DuPont chemist who could help if we have any further questions. Glad to hear you have made some very good progress. Not sure how much we need, however more is better so we can share it with others.

Mark

From: Zhang, Zhenfa <<u>zhenfaz@email.unc.edu</u>> Sent: Monday, January 28, 2019 11:55 AM

To: Strynar, Mark < strynar.mark@epa.gov; Surratt, Jason D. < surratt@unc.edu; Lang, Johnsie

<lang.johnsie@epa.gov>

Cc: Bodnar, Wanda M < wanda bodnar@unc.edu>

Subject: RE: update on synthesis

Hi Mark,

Thank you for coping me in your message. I assume I started with the same monomer precursor you acquired(CAS4089-58-1), it took quite some time for us to get that. I actually spent that time trying to make that monomer precursor myself while I was waiting for that to come, but stopped doing that after I got it from the supplier. The monomer precursor is not so easy to make pure in small quantity so I think it is better to leave that to the supplier if we don't have to work with large quantity.

Since I talked with Jason the other day, I am pleased to see some more progress is made with the synthesis of Nafion BP2, and I got some product already as I told Jason last week. It still needs some final purification and characterization. Basically put a number on the purity. There is some diglyme solvent that is surprisingly resistant to freeze dry. After tested some solvent extraction and failed to improve, I repeatedly did freeze dry. Calculated from NMR that is just a few percent, so I guess we will live with it for now, till we find a way to improve later on. For that matter, I am just trying to find an internal standard for NMR calculation of purity, we can have your precursor if you still have some since I exhausted ours unware of the need in the beginning. Thanks,

Zhenfa

From: Strynar, Mark <<u>Strynar.Mark@epa.gov</u>> Sent: Monday, January 28, 2019 8:47 AM

To: Surratt, Jason D. <<u>surratt@unc.edu</u>>; Lang, Johnsie <<u>lang.johnsie@epa.gov</u>>

Cc: Bodnar, Wanda M <wanda bodnar@unc.edu>; Zhang, Zhenfa <zhenfaz@email.unc.edu> Subject: RE: update on synthesis

Jason,

Back to work today and hoping to pick this up. We have acquired 5 grams of the Nafion Monomer precursor we think would make the synthesis to Nafion BP2 easier.

Lets have a chat when you get a chance.

Mark

From: Surratt, Jason D. <surratt@unc.edu> Sent: Wednesday, January 09, 2019 1:27 AM

To: Strynar, Mark <strynar.mark@epa.gov>; Lang, Johnsie <lang.johnsie@epa.gov>

Cc: Bodnar, Wanda M <wanda bodnar@unc.edu>; Zhang, Zhenfa <zhenfaz@email.unc.edu>

Subject: update on synthesis

Hi Mark,

Hope this email finds you well and happy new year! I'm finally back to work this week! I took a couple of weeks off to travel and be with family during the latter part of last year.

I spoke with Zhenfa here at UNC. As you know, he is our in house organic synthetic chemist. He has been working on the synthesis of Nafion BP2. Right now he tells me he is very close to getting the Nafion BP1 compound; however, as you know the Nafion BP2 is much more difficult. He is getting more confident though that he will be able to get to Nafion BP2. As of right now, we can't say an exact date as to when we can get enough material in high purity to share.

How much of the Nafion BP2 were you hoping to get? I know you are also interested to know the exact method he develops for getting Nafion BP2. I think you also have interest in doing this synthesis yourself at EPA.

Best wishes to you, Jason

Jason D. Surratt, Ph.D. Professor

Program Director of the N.C. Per- and Polyfluoroalkyl Substance Testing (PFAST) Network Co-Director, Undergraduate Studies, Environmental Sciences & Engineering

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